STM and *ab initio* study of holmium nanowires on a Ge(111) Surface

C. Eames, C. Bonet, M. I. J. Probert and S. P. Tear*

Department of Physics, University of York, York YO10 5DD, United Kingdom

E. W. Perkins

School of Physics and Astronomy, University of Nottingham, Nottingham NG7 2RD, United Kingdom

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A nanorod structure has been observed on the Ho/Ge(111) surface using scanning tunneling microscopy (STM). The rods do not require patterning of the surface or defects such as step edges in order to grow as is the case for nanorods on Si(111). At low holmium coverage the nanorods exist as isolated nanostructures while at high coverage they form a periodic 5×1 structure. We propose a structural model for the 5×1 unit cell and show using an *ab initio* calculation that the STM profile of our model structure compares favourably to that obtained experimentally for both filled and empty states sampling. The calculated local density of states shows that the nanorod is metallic in character.

Self-assembled nanorods on surfaces have potential applications in optoelectronic and microelectronic devices and some interesting properties have already been reported for such structures [1, 2, 3].

On the Si(001) surface self-assembled nanorods have been observed for many adsorbates including the group III-IV metals (Ref. [4] and references therein) and the rare-earth (RE) metals ([5, 6, 7, 8] and references therein). The Si(111) surface has threefold symmetry and is not as favourable a host to nanorod growth. Gd and Pb nanorods have been grown in the lee of step edges along the [110] direction [9, 10]. On the terraced regions the way forward is to deposit an adsorbate on a prestructured adsorbate/Si(111) surface. In this way Pb nanorods have recently been grown on the Sm/Si(111) surface [11].

Germanium is attracting renewed interest as a semiconductor because it possesses a high hole carrier mobility. On Ge(001) no nanowires involving RE metals have been reported. On Ge(111) a one monolayer (ML) deposit of a RE metal forms a two-dimensional 1×1 structure [12] after annealing at $\approx 500\,^{\circ}$C. A similar structure is formed in Si(111)1×1 RE systems (Ref. [13] and therein). Pelletier *et al.* briefly noted the formation of metastable rod like structures on the Er/Ge(111)-c(2×8) coexisting with the 1×1 structure [14].

In this paper we report the formation of holmium nanorods on the Ge(111) surface which we have observed in a STM experiment and whose structure and properties we have investigated using an *ab initio* density functional theory calculation. We have deposited low coverages (0.1-0.15 ML) of Ho onto a clean substrate held at 250°C and instead of the 1×1 structure we observe a series of isolated holmium nanorods. These are true isolated nanostructures because they are not part of a periodic reconstruction or rectangular islands. The nanorods have a constant width that is very narrow compared to other nanorod structures and they do not require step edges or patterning in order to form. When the experi-

ment is repeated using a higher Ho coverage the nanorods exist as part of a periodic 5×1 structure. We have performed a medium energy ion scattering (MEIS) study and used this in conjunction with the STM data to parameterise the structure to the extent that we can suggest a quantitative model for the 5×1 unit cell. The simulated STM for the model structure is qualitatively compared to the STM images obtained in the laboratory and the comparisons are favourable.

The STM experiments were done with an Omicron Nanotechnology GmbH microscope at a typical UHV base pressure of $\leq 2 \times 10^{-10}$ mbar. The germanium substrate was cleaned by argon ion bombardment followed by annealing at $\approx 500\,^{\circ}$C for about 15 minutes and *in situ* low-energy electron diffraction was used to check that a clean Ge(111)-c(2×8) surface had been made.

The sample was prepared by depositing 0.1 ML of Ho from a quartz crystal calibrated evaporation source onto a clean Ge(111)-c(2×8) surface held at a temperature of $\approx 250\,^{\circ}$C that was monitored using a k-type thermocouple attached to the sample stage. Figure 1 shows a STM image of a large area on the surface. Isolated and well defined nanorods have formed on flat regions clear of step edges on a surface that was not patterned or prestructured in any way. The rods typically extend for ≈ 40 nm and they have a constant width. The structures have been reproduced in several experiments.

At a higher Ho coverage of 0.25 ML the rods stack in close parallel proximity, forming small islands comprised of a periodic 5×1 structure of which the isolated nanorods are a precursor. The dimensions of the 5×1 unit cell were measured using surrounding areas of Ge(111)-c(2×8) for internal calibration. Figure 2(a) shows a filled states image of a region 4.2 × 3.3 nm^2 in size that contains two nanorods separated by a small gap taken from a region that comprises seven nanorods side by side. The atoms within each nanorod appear to occupy two distinct levels. With respect to the Ge rest atom of the surrounding c(2×8) reconstruction the height of the lower level is 2.1
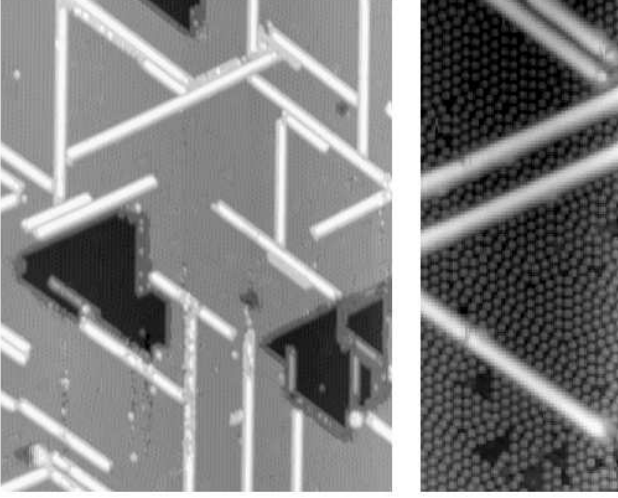
FIG. 1: Two overview STM images of the nanorods formed with a low (0.1 ML) coverage of Ho. (Left) Large area (59 × 75 nm^2) filled states image taken with a sample bias of -2.0 V and a tunneling current of 2 nA. (Right) 14 × 33 nm^2 empty states image taken with sample bias $+2.0$ V and a tunneling current of 2 nA showing the surrounding clean Ge(111)-$c(2\times8)$ with some domains of (2×2) and $c(4\times2)$ that are typically present on this substrate.

(a) Filled states experiment.

(b) Filled states theory.

FIG. 2: Measured (a) and simulated (b) filled states STM images for the Ge(111)5×1-Ho system. The tunneling current in the experiment was 2 nA. Both images correspond to a sample bias of -2.0 V and the image dimensions are 4.2 × 3.3 nm^2.
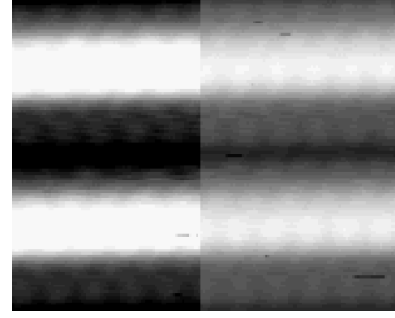
Å and that of the nanorod peak is 3.9 Å. The width of the lower layer is 1.7 nm.

Figure 3(a) shows an empty states STM image of a region 4.2 × 3.3 nm^2 in extent. Features within the top layer of the nanorod can now be resolved, especially when the image contrast is adjusted as in the left half of the figure. In the empty states STM images the top layer of the nanorod was measured as being 3.1 Å above the Ge adatom layer (and thus 3.8 Å above the rest atom layer since the adatom layer is known to be 0.66 Å above the rest atom layer [15]).
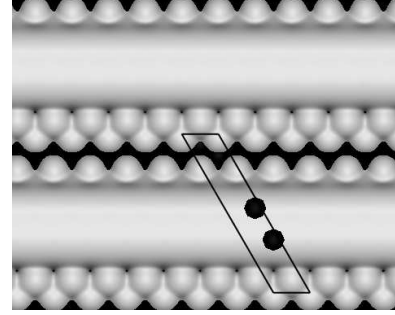
Whilst we cannot claim that our layer height measurements correspond to pure topography with no contribution from electronic effects, the consistency of the filled and empty states measurements and the large height difference of 3.8-3.9 Å from the nanorod peak to the Ge rest atoms allow us to conclude that any model of the nanorod should involve a two-layer structure.

A MEIS experiment in which incident H$^+$ ions were strongly scattered in all directions by the Ho atoms was carried out at the CCLRC Daresbury UK MEIS facility. The ion flux scattered from Ho atoms did not show any dips at any emergent angle which might indicate blocking by Ge atoms in a layer above the Ho atoms. We thus interpret the two "bright" features per 5×1 unit cell in the empty states STM images as being associated with holmium atoms forming the upper layer of the nanorod.

The Ge atoms in the lower level of the nanorod,

2.1 Å above the rest atoms of the $c(2\times8)$ reconstruction, appear to be too low to be a full Ge bilayer (which would have a 3.27 Å step height [15]) and a STM image (not shown) in which nanorods can be seen on adjacent terraces separated by a monoatomic step supports this conclusion. Consideration of the bonding requirements of the two trivalent Ho atoms per 5×1 unit cell also leads to the conclusion that Ho atoms cannot be adsorbed atop a simple bulk-terminated Ge surface since in such a situation the Ge surface would provide only 5 dangling bonds to be quenched by the two trivalent Ho atoms.

On the other hand, the lower layer of the nanorod is too high above the rest atoms of the Ge substrate to be a simple adatom layer (0.66 Å above the rest atoms in clean Ge(111)-$c(2\times8)$ [15]). A visual comparison with surrounding areas of the $c(2\times8)$ reconstruction in the empty states STM images suggests an atomic density in the lower nanorod layer which is greater than that of a dilute (e.g. 2×2) adatom layer. Further information was obtained from our STM observations of occasional faulted nanowire growth in which the topmost Ho layer was sometimes absent from the nanorod over a small region. Under these conditions the Ge layer was found to be continuous across the width of the nanorod, extend-
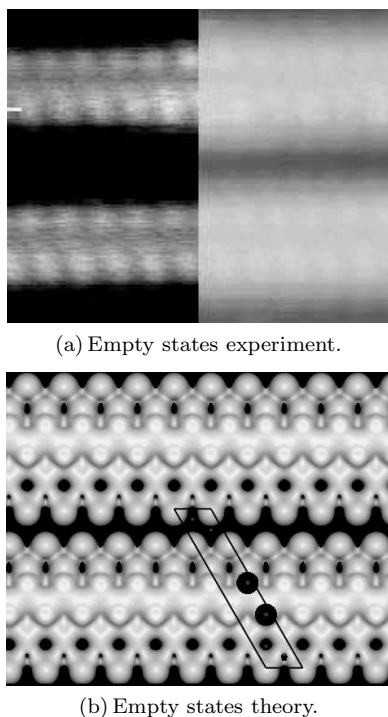
(a) Empty states experiment.

(b) Empty states theory.

FIG. 3: Measured (a) and simulated (b) empty states STM images for the Ge(111) 5×1 Ho system. The tunneling current in the experiment was 2 nA. Both images correspond to a sample bias of + 1.50 V and the image dimensions are 4.2 × 3.3 nm². The left half of (a) has been contrast adjusted so that the Ho atoms within the top layer of the nanorod can be more clearly discerned.

(a) Top view.

1.7nm

(b) Side view.

FIG. 4: Two views of the Ge(111)5×1-Ho system; (a) top view in which the 5×1 unit cell is outlined in black (b) side view. Large black atoms are Ho, dark grey is reconstructed Ge and light grey is bulk like Ge.

ing across the area that would normally be covered by the upper Ho layer. The lower level of the nanorod was therefore identified as consisting of a single layer of additional Ge atoms (with density around one monolayer) atop the first bulk like Ge bilayer.

Given these considerations we propose the structure that is shown in figure 4 in which there is a Ho nanorod atop an almost flat Ge layer atop a bulk like Ge substrate. The structural parameters of the 5×1 supercell are available upon request.

To validate the structural model we have calculated the STM image that it would be expected to produce using the CASTEP *ab initio* density functional theory based code [16]. The generalised gradient approximation was used to model exchange and correlation effects. The electronic wave function was expanded in a plane wave basis set with a cutoff energy of 360 eV. The ionic cores were represented with ultrasoft pseudopotentials. In reciprocal space the wave function was sampled at eight points arranged in a Monkhorst-Pack grid [17]. The atomic positions in the experimentally suggested model were varied until the local energy minimum was found and the expected constant current STM profile was obtained from the electronic structure using the Tersoff-Hamann scheme
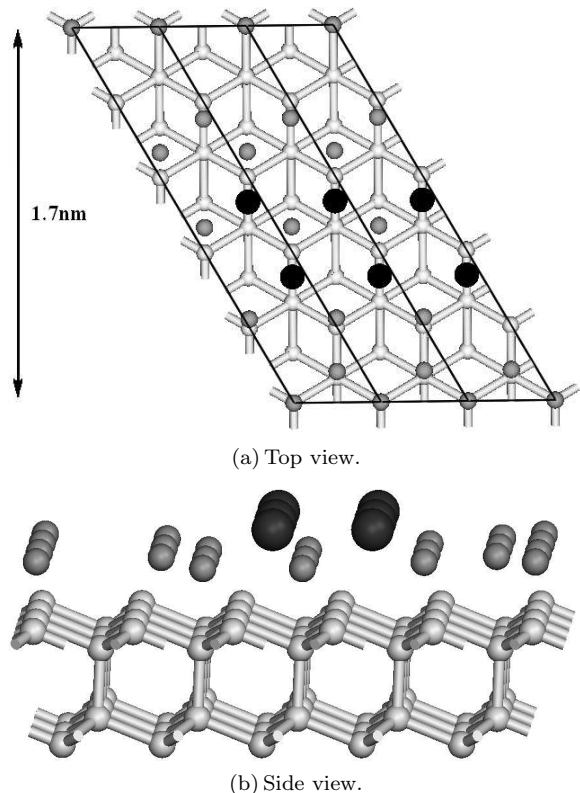
[18].

Figure 2(b) shows the filled states image so obtained at a sample bias of −2.0 V. The image dimensions are 4.2 × 3.3 nm² and it can be directly compared with the experimental result in figure 2(a). The dominance of Ho in the nanorod is evident in the modelled system. There are many filled electronic states around the high-valency holmium atoms that have a favourable probability for tunneling into the tip. The trenchlike structure between the nanorods does indeed seem to be formed by the arrangement of Ge that we have suggested.

Figure 3(b) shows the empty states image calculated with a sample bias of +1.5 V. The image dimensions are 4.2 × 3.3 nm² and it can be directly compared with the experimental result in figure 3(a). Atomic resolution within the nanorod is apparent in the theoretical image as it was in the experiment. Between the nanorods we see the structure in the germanium underlayers that was not accessible in the experiment.

The electronic structure can be used in conjunction with population analysis to determine the bonding environment responsible for the nanorod structure. Figure 5 shows three slices through the electronic density, one in the plane of the Ge flat layer and two vertical slices

through the two holmium atoms. There is a mixture of covalent and ionic bonding within the nanorod reflecting the large contribution of electron transfer from the Ho atoms.
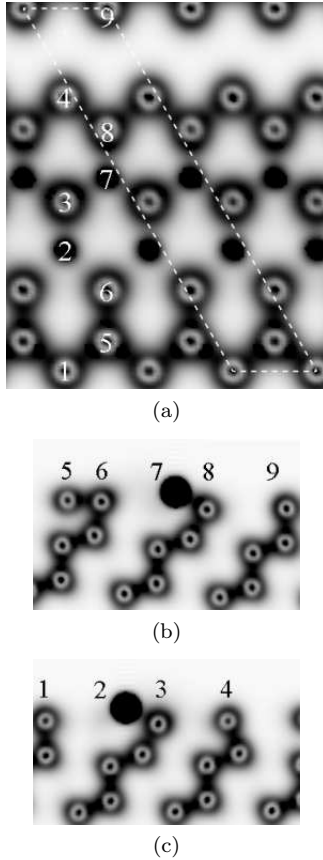

(a)

(b)

(c)

FIG. 5: Electron density within a slice taken (a) horizontally in the plane of the surface through the flat layer of Ge atoms (b)/(c) vertically through the two Ho atoms (labelled 2 and 7) to show the bonding to the layer below.

In figure 5 Ge atom 3 is covalently bonded to the two Ho atoms and to the Ge atom in the layer below in a tetrahedral arrangement and this atom has negligible extra charge transferred from either Ho atom. There is a significant amount of charge transfer from Ho 2 to germanium 6 and to a lesser extent Ge 5 and Ge 1 near to the edge of the shelf. Ge 5 is sp^2 hybridised and we can see three planar trigonal bonds in the overhead view and no bonds to the layer below in the side view. There is also a significant amount of charge transfer from Ho 7 to Ge 8 and to a lesser extent to Ge 4. Ge 1 and Ge 4 are partially sp^2 hybridised with some remainder of tetrahedral bonding. Charge transfer from the two Ho atoms seems to be a key element in the stability of this system.

The electronic properties of the nanorods can be predicted from the results of the *ab initio* calculation. In figure 6 the local density of states within the nanorod is shown. The spike in the electronic population at energies close to the Fermi level indicates the metallic character of the nanorod and confirms the decoupling of its electronic states from those in the semiconducting germanium bulk.
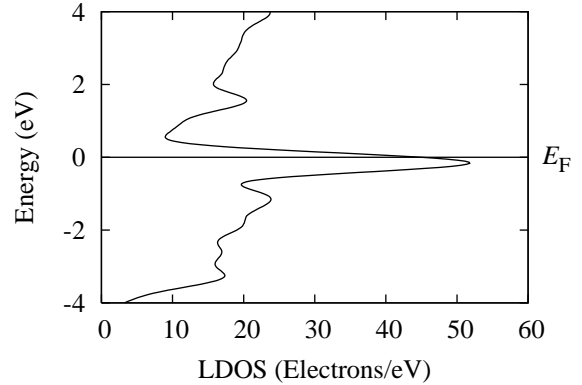

FIG. 6: The calculated total local density of states for the nanorod structure. There is a large concentration of states close to the Fermi level that are thermally accessible that render the system metallic.

Scanning Tunneling Spectroscopy data taken from the surface supports this. Figure 7 shows tunneling current measurements taken from the nanorod and from the surrounding Ge substrate for reference. The nanorod clearly has conducting states at the Fermi level whereas the band gap of the Ge substrate means that it has no conducting states at the Fermi level.
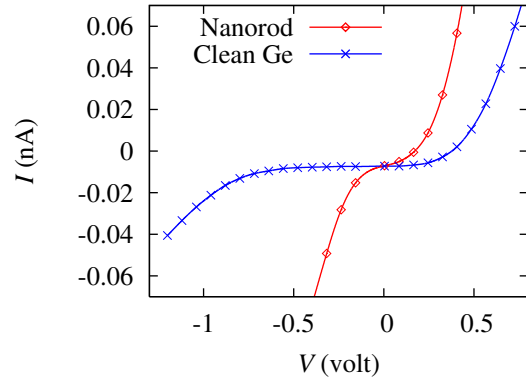

FIG. 7: (Colour online) Experimental STS data showing the conducting properties of the nanorod. Data taken from the Ge substrate, with its large band gap at the Fermi level, is included for reference.

In conclusion, nanorods have been formed by depositing a low coverage of Ho on the Ge(111) surface. These are a true isolated nanostructure because they are not part of a periodic reconstruction or rectangular islands. The nanorods have constant width that is very narrow compared to other nanorod structures and they do not require step edges or patterning in order to form. When the experiment is repeated using a higher Ho coverage

the nanorods exist as part of a periodic 5×1 structure. We have introduced a model for this structure which we have quantitatively validated using an *ab initio* geometry optimisation. We have shown that in both filled and empty states imaging the calculated STM profile for this model is in good qualitative agreement with experiment and the calculated electronic structure suggests that the nanorod is metallic in character and can be termed a nanowire.

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* Corresponding author. E-mail: spt1@york.ac.uk

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